

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 82200638.3

(51) Int Cl.<sup>3</sup>: C 08 C 19/44

(22) Date of filing: 25.05.82

(30) Priority: 15.06.81 US 274111

(43) Date of publication of application:  
22.12.82 Bulletin 82/51

(84) Designated Contracting States:  
BE DE FR GB IT NL SE

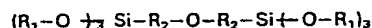
(71) Applicant: SHELL INTERNATIONALE RESEARCH  
MAATSCHAPPIJ B.V.  
Carel van Bylandtlaan 30  
NL-2596 HR Den Haag(NL)

(72) Inventor: Haynes, George Rufus  
11706 Gardenglen Drive  
Houston Texas 77070(US)

(74) Representative: Puister, Antonius Tonnies, Mr. et al.  
P.O. Box 302  
NL-2501 CH The Hague(NL)

(54) Multifunctional coupling agent.

(57) Lithium metal-terminated polymers of one or more alkadienes, or of one or more alkadienes and one or more monoalkenyl arenes are coupled by reaction with a coupling agent of the general formula:



where  $R_1$  is an alkyl group of 1 to 4 carbon atoms and  $R_2$  is an alkyl group of 2 to 10 carbon atoms.

EP 0 067 468 A2

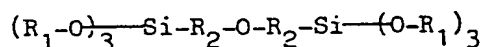
## MULTIFUNCTIONAL COUPLING AGENT

The present invention relates to a process for the production of a polymer comprising reacting a living lithium-terminated polymer having the formula  $P-Li$ , wherein  $P$  is selected from the group consisting of polymer chains of one or more alkadienes having 4-12 carbon atoms and copolymer chains of one or more alkadienes having 4-12 carbon atoms and one or more monoalkenyl arenes of 8-16 carbon atoms, having the alkenyl radical attached to an arene ring carbon atom, with a polyalkoxy silane coupling agent.

Polymethoxy silanes have been disclosed in U.S. P. 3,880,954 and glycidoxy-polyalkoxy silanes are known from U.S. P. 4,185,042 wherein methyl trimethoxy silane has been compared with gamma-glycidoxypropyl trimethoxy silane (GPTS).

A new coupling agent has now been discovered that results in polymers having good coupling efficiencies along with an excellent property balance in footwear compositions.

The present invention comprises a process for the production of a polymer comprising reacting a living lithium-terminated polymer having the formula  $P-Li$  wherein  $P$  is selected from the group consisting of polymer chains of one or more alkadienes having 4-12 carbon atoms and copolymer chains of one or more alkadienes having 4-12 carbon atoms and one or more monoalkenyl arenes of 8-16 carbon atoms, having the alkenyl radical attached to an arene ring carbon atom, with a polyalkoxy silane coupling agent, characterized in that the polyalkoxy silane has the general formula:



where  $R_1$  is an alkyl group of 1 to 4 carbon atoms and  $R_2$  is an alkyl group of 2 to 10 carbon atoms.

The coupling agents according to the present invention have a number of advantages. For one, the associated coupling efficiency is greater than 95%, which is a very high coupling efficiency. Further, compositions made with the resulting  
5 polymer have a much improved tear strength, tensile strength and flex crack resistance when compared to compositions containing polymers made with other methoxy silane coupling agents, such as GPTS.

The coupled polymers of the invention also have better  
10 heat stability than GPTS coupled materials. Thus, the subject polymers can be finished without significant degradation under conditions which appreciably degrade the GPTS coupled polymers. The heat stability test included heating about 0.5 gram samples sealed in aluminium sheet for two minutes at 216-246°C. The  
15 greater heat stability will also result in less degradation during compounding and moulding operations.

The preferred group of acyclic conjugated alkadienes that can be polymerized into the polymer chain P are those containing 4-8 carbon atoms. Examples for such alkadienes are 1,3-butadiene,  
20 2,3-dimethyl-1,3-butadiene, piperylene, 3-butyl-1,3-octadiene, isoprene, 2-phenyl-1,3-butadiene. Preferred are isoprene and 1,3-butadiene.

The molecular weight of the alkadiene block may vary from 3,000 to 500,000, preferably from 10,000 to 250,000.

25 Monoalkenyl arenes that can be polymerized together with the alkadienes to form the polymer chain P preferably are those selected from the group of styrene, the methylstyrenes, particularly 3-methylstyrene, the propylstyrenes, particularly 4-propylstyrene, vinylnaphthalenes, particularly 1-vinyl-  
30 naphthalene, cyclohexylstyrenes, particularly 4-cyclohexylstyrene, p-tolylstyrene, and 1-vinyl-5-hexylnaphthalene. Preference is given to styrene.

The molecular weight of the monoalkenyl arene block may vary from 2,000-100,000, preferably from 5,000 to 75,000.

The polymer chains P can be homopolymers of the alkadiene monomers defined or can be random, tapered or block copolymers of alkadiene monomers and monoalkenyl-substituted aromatic monomers. Such a block copolymer exhibits properties both of an elastomer and of a thermoplastic polymer provided that the alkadiene block is coupled to the coupling agent. The presently preferred polymer chains P are those in which the conjugated dienes are present in a major amount and the monovinyl-substituted arenes are present in a minor amount.

10       The molecular weight of the polymers of this invention can vary in broad ranges. For the usual applications of the coupled polymers, the number average molecular weight will be in the range of about 6,000 to about 2,000,000, preferably 40,000 to 1,000,000.

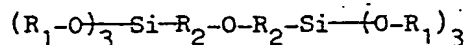
15       The living lithium-terminated polymer according to the present invention is prepared by methods known in the art, e.g. U.S. P. 4,185,042. The lithium-based initiator systems used in the first step of the process to make the coupled polymers of this invention are those known in the art, such as isopropyllithium, 20   n-butyllithium and sec.-butyllithium.

      The polymerization reaction is carried out in the presence of a hydrocarbon diluent. Preferably, the hydrocarbon diluent is a paraffinic, cycloparaffinic or aromatic hydrocarbon having 4-10 carbon atoms or a mixture of such diluents.

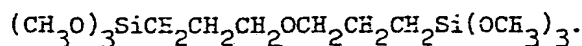
25       The quantity of coupling agent employed with respect to the quantity of living polymers P-Li present depends largely upon the degree of coupling and the properties of the coupled polymers desired. Preferably, the coupling agent defined above will be employed in a range of about 0.1 to about 0.5, preferably about 0.2 to about 0.3 moles of coupling agent based upon 30   the moles of lithium metal present in the polymer. The number of arms obtained for the coupled polymers depend upon the ratio of coupling agent to lithium in the living polymer. About 0.2 moles of coupling agent per mole lithium will generally

give largely 4 arms, with some 3-arm and some greater than 4-arm polymers also. About 0.3 mole coupling agent per mole lithium will give mostly 3- and 4-arm polymers.

As stated above, the coupling agent of the present invention is a silane having the general formula:



where  $R_1$  is an alkyl group of 1 to 4 carbon atoms and  $R_2$  is an alkyl group of 2 to 10 carbon atoms. Preferably,  $R_1$  is a methyl group and  $R_2$  is a propyl group. Therefore, the preferred coupling agent is 3,3'-oxydipropyl-bis(trimethoxy silane), which has the formula:



The temperature at which the coupling reaction is carried out can vary over a broad range and, for convenience, often is the same as the temperature of polymerization. Although the temperature can vary broadly from about 0° to 150°C, it will preferably be within the range from about 20°C to 100°C.

The coupling reaction is normally carried out by simply mixing the coupling agent, neat or in solution, with the living polymer solution. The reaction period is usually quite short. The normal duration of the coupling reaction will be in the range of 1 minute to 1 hour. Longer coupling periods may be required at lower temperatures.

After the coupling reaction, the coupled polymers are recovered by treating the reaction mixture with terminating agents containing active hydrogens such as alcohols or water or aqueous acid solutions or mixtures thereof. It is usually preferred to add an anti-oxidant to the reaction mixture before isolation of polymer.

The polymer is separated from the reaction mixture by standard techniques, such as steam stripping or coagulation with a suitable non-solvent such as an alcohol. The coagulated or stripped polymer is then removed from the resulting medium by, e.g., centrifugation or extrusion. Residual solvent and

other volatiles can be removed from the isolated polymer by heating, optionally under reduced pressure or in a forced air flow.

5 Styrene-butadiene block copolymers prepared according to the present invention may be compounded with various other ingredients, thereby forming compositions eminently suitable for footwear applications. These footwear compositions generally comprise a block copolymer component (i.e., the polymer according to the present invention), a thermoplastic polymer com-  
10 ponent, plasticizers, and fillers.

An important blending component is the thermoplastic polymer. In the present specification and claims, the term "thermoplastic polymer" is distinguished from the term "thermoplastic elastomer" or "thermoplastic rubber" in that the thermoplastic polymers are  
15 defined as non-elastomeric polymers. These thermoplastic polymers have the generally well-known characteristics of ordinary thermoplastics and include poly(styrene), poly(ethylene), poly(propylene) and copolymers of ethylene and vinyl acetate. The amount of thermoplastic polymer typically em-  
20 ployed varies from about 5-150 phr, preferably about 50-115 phr. The term "phr" is well known, and means parts by weight per 100 parts by weight rubber (or block copolymer as in the present case).

Plasticizers are also employed in the compositions. Pre-  
25 ferred plasticizers are hydrocarbon rubber extending oils. These hydrocarbon rubber extending oils, usually referred to as paraffinic/naphthenic oils, are usually fractions of refined petroleum products having less than about 30% by weight of aromatics (by clay-gel analysis) and usually have viscosities  
30 between about 100 and 500 SSU at 38°C. Commercial extending oils include SHELLFLEX<sup>®</sup> oils, Nos. 310, 371 and 311 (which is a blend of 310 and 371). The amount of extending oil employed varies from about 5-175 phr, preferably from about 50-160 phr.

Additional resins are also employed in the present compositions. The additional resins employed herein are high softening point resins that are compatible with the monoalkenyl end blocks of the block copolymer and include polymers of alpha-methyl styrene, copolymers of  
5 alpha-methyl styrene and vinyltoluene, coumaroneindene resins, polyindene resins, and poly(methylindene) resins. The amount of end block compatible resin employed varies from about 0-90 phr, preferably 5-40 phr.

The fillers used in the present compositions are well known in the art and include clay, talc, titanium dioxide, carbon black,  
10 calcium carbonate, silica, and other pigments as well as fibrous fillers such as cellulosic fibres, sawdust, ground cork, etc. Preferred fillers include clay, talc, silica and calcium carbonate. The amount of filler employed varies from 0-150 phr, preferably 5-110 phr. Additional minor amounts of anti-oxidants, ultra-violet stabilizers,  
15 fire retardants and the like may also be added.

The various components may be mixed together in a variety of processes. One preferred process is the dry blending process of U.S. patent No. 4,060,510, the disclosure of which is herein incorporated by reference.

20 The invention is further illustrated by reference to the following Examples, which are given for the purposes of illustration only, and are not meant to limit the invention to the particular reactant and conditions employed therein.

#### EXAMPLE I

25 A precursor block copolymer was prepared in cyclohexane solvent utilizing sec.-butyl lithium as the initiator by first polymerizing styrene at 30-60°C to form a polystyrene block and thereafter injecting butadiene to form a butadiene block, the living block copolymer so formed then having the structure polystyrene-polybuta-  
30 diene-lithium. It was determined that this precursor block copolymer had average molecular weights in the polystyrene block of about 13,000 and that the polybutadiene block had an average molecular weight of about 25,000. A portion of the precursor block copolymer (equivalent to 0.9 gram-moles of lithium) was reacted for 20 minutes  
35 at 60°C with 0.22 gram-moles of 3,3'-oxydipropyl-bis(trimethoxy silane) referred to as "ODPTS". About 95 to 98% of the intermediate polymer (polystyrene-polybutadiene-lithium) was coupled to form the

the desired end product. The end product had a total molecular weight (calculated from polystyrene equivalent) of about 160,000 and a functionality of about 4.

#### EXAMPLE II

5        The polymer from Example I was then compounded in a foot-  
wear formulation with a hydrocarbon extending oil, silica  
filler, a dimethyl adipate-coupled styrene-butadiene block  
copolymer, high density polyethylene, flock and an anti-oxidant/  
U.V. stabilizer package. This formulation was then compared  
10 with a similar formulation containing identical ingredients and  
amounts except for the silane coupled styrene-butadiene block  
copolymer. The styrene-butadiene block copolymer employed for  
comparison purposes was prepared with a ~~gamma~~-glycidoxypyrpyl-  
trimethoxy silane (GPTS) coupling agent. The results are presented  
15 below in Table I.

TABLE I  
Compound properties of polymer

Test	Polymer made with GPTS coupling agent (control)	Polymer made with ODPTS coupling agent (according to the in- vention)
Melt flow, Cond. E, g/10 min.	13.8	7.4
Hardness, Shore A, compression moulded, instantaneously/after 10 sec.	53/51	55/54
Stiffness, Tinius Olsen, kg/cm <sup>2</sup>	47	60
Tear strength, trouser, $\parallel/\perp$ , kg/cm	8.1/8.5	10.8/12.6
Flex crack resistance, kilocycles to 500% growth	734	1481
Taber abrasion, cm <sup>3</sup> loss/kilocycle	0.4428	0.3363
Adhesion (peel strength), kg/cm	6.6	7.0
Tensile strength, $\parallel/\perp$ , kg/cm <sup>2</sup>	29/30	41/44
Elongation, $\parallel/\perp$ , %	620/660	715/760
300% Modulus, $\parallel/\perp$ , kg/cm <sup>2</sup>	19/14	16/14
Set, $\parallel/\perp$ , %	17/15	18/18



The above data were obtained using polymers having equivalent coupling yields. The lower flow for the ODPTS polymer reflects its greater number of arms (4) compared to about 3.2 for the GPTS coupled polymer. The greater strength properties for the ODPTS coupled polymer is shown in the flex crack resistance, which is twice that for the GPTS coupled polymer, and in the about 40% improvement in tear strength and tensile strength. The smaller loss from abrasion for the ODPTS coupled polymer (only 76% of that for the GPTS coupled polymer) indicates better wear properties and longer service life. The greater elongation for the ODPTS coupled material shows that it can be stretched further without breaking. These properties all contribute towards a better wearing, longer lasting finished product in use.

BAD ORIGINAL

C L A I M S

1. A process for the production of a polymer comprising reacting a living lithium-terminated polymer having the formula P-Li, wherein P is selected from the group consisting of polymer chains of one or more alkadienes having 4-12 carbon atoms and copolymer chains of one or more alkadienes having 4-12 carbon atoms and one or more monoalkenyl arenes of 5-18 carbon atoms, having the alkenyl radical attached to an arene ring carbon atom, with a polyalkoxy silane coupling agent, characterized in that the polyalkoxy silane has the general formula:
- $$(R_1O)_3-Si-R_2-O-R_2-Si-(O-R_1)_3$$
- where  $R_1$  is an alkyl group of 1 to 4 carbon atoms and  $R_2$  is an alkyl group of 2 to 10 carbon atoms.
2. The process according to claim 1, characterized in that the alkadiene is isoprene or butadiene and the monoalkenyl arene is styrene.
3. The process according to claim 1, characterized in that P is a polymer chain of one or more alkadienes selected from the group consisting of butadiene and isoprene.
4. The process according to claim 1, characterized in that P is a block copolymer of styrene and butadiene with the butadiene block being attached to the lithium ion and having a molecular weight of from 10,000 to 250,000 and with the styrene block having a molecular weight of from 5,000 to 75,000.
5. The process according to claim 1, characterized in that  $R_1$  is a methyl group and  $R_2$  is a propyl group.
6. The process according to claim 4, characterized in that  $R_1$  is a methyl group and  $R_2$  is a propyl group.

7. The polymer produced by the process of claim 5 or 6.
8. The polymeric composition comprising the polymer produced by the process of claim 4, a thermoplastic polymer, a filler and a plasticizer.

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**